Notes

Synthesis and Spectroscopy of Halogenated Cyclopentasilanes

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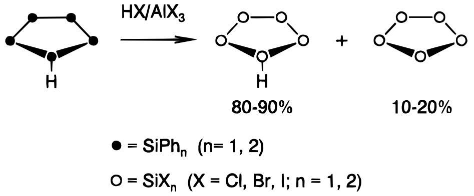
Summary: Nonahalocyclopentasilanes, HSi_5X_9, and octahalocyclopentasilanes, $H_2Si_5X_8$ (X = Cl, Br, I), were prepared by dearylation of the corresponding phenylated cyclosilanes HSi_5Ph_9 and $H_2Si_5Ph_8$ with gaseous hydrogen halides and catalytic amounts of aluminum halides (HX/AlX_3) dissolved in benzene. The products were identified and characterized by IR and NMR spectroscopy (^1H and ^{29}Si, including Si−H and Si−Si coupling constants). The halogenation of trans-1,3-$H_2Si_5Ph_8$ led to isomeric mixtures of cis-1,3-$H_2Si_5X_8$ and trans-1,3-$H_2Si_5X_8$ in equimolar amounts.

Introduction

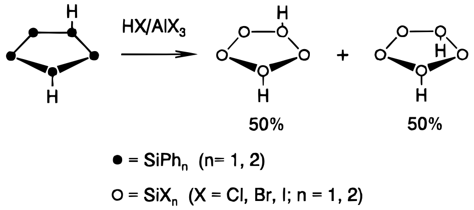
The first synthesis of a perhalogenated cyclosilane, prepared by dearylating Si_5Ph_{10} with HBr, was reported in the early seventies by Hengge et al.[1] The hydrogenation of Si_5Br_{10} led to the first unsubstituted cyclosilane, Si_5H_{10}.[1] Catalytic dearylation of perphenylated cyclosilanes with gaseous HCl and HI using the respective aluminum halides as catalysts also allowed the preparation of $(Cl_2Si)_m$[2] and $(I_2Si)_m$,[3] with $m = 4$, 5, or 6. For Si_5Cl_{10}, Si_5Br_{10}, and Si_5I_{10} UV/vis,[4] IR, and Raman spectra were measured and normal coordinate analyses[5] and empirical force-field calculations[6] were performed. The crystal structures of Si_5Br_{10} and Si_5I_{10} were determined.[7] The preparation of the nonahalocyclopentasilanes HSi_5Cl_9 and HSi_5Br_9 was first reported by Stüger et al., who utilized these compounds for the synthesis of various bis(cyclopentasilanyl) derivatives.[8]

By means of NMR, IR, and Raman spectroscopy at low temperatures accompanied by ab initio calculations, we are planning to investigate partially halogenated and other selectively functionalized cyclosilanes with respect to molecular dynamics (conformational changes such as the pseudorotation of cyclopentasilanes and the ring flip of cyclotetrasilanes). For this purpose we have already prepared and characterized a number of mono- and difunctional phenylated cyclopentasilanes[9] and monofunctional arylated cyclotetrasilanes.[10]

Scheme 1



Scheme 2



Results and Discussion

The nonahalocyclopentasilanes HSi_5Br_9 (**4**) and HSi_5I_9 (**5**) were synthesized by catalytic halogenation of HSi_5Ph_9 (**1**) with HX/AlX_3 in benzene (Scheme 1); the completeness of dearylation was controlled by IR spectroscopy. **4** was obtained as a highly viscous oil which partially solidified in microcrystalline structures, whereas **5** precipitated as a crystalline solid. Due to the substitution of hydrogen by halogen atoms, 10−20% of the perhalogenated cyclosilanes were obtained as byproducts in both cases. This side reaction could not be avoided by the modification of the reaction conditions nor by the use of liquid halogen halides under pressure instead of HX/AlX_3. The synthesis of HSi_5Cl_9 (**3**) and **4** by dearylation of **1** with liquid HCl and HBr, respectively, was reported by Stüger et al., who obtained similar percentages of perhalogenated byproducts.[4] The NMR data for **3**−**5** are summarized in Tables 1 and 3; the perhalogenated byproducts' ^{29}Si chemical shifts (ppm) relative to TMS are −1.9 for Si_5Cl_{10}, −28.2 for Si_5Br_{10}, and −98.0 for Si_5I_{10}.

The octahalocyclopentasilanes $H_2Si_5Cl_8$ (**6**), $H_2Si_5Br_8$ (**7**), and $H_2Si_5I_8$ (**8**) were prepared by halogenation of

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Table 1. ^{29}Si NMR Data for the Nonahalocyclopentasilanes, HSi_5X_9 (3−5; X = Cl,[4] Br, I)

compd no.	X	Si(1)		Si(2,5)		Si(3,4)	
		δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)
3	Cl	−27.6	$^1J_{Si-H}$ 255.2	1.8	$^2J_{Si-H}$ 8.2	−2.1	$^3J_{Si-H}$ 7.7
4	Br	−43.7	$^1J_{Si-H}$ 255.0 $^1J_{Si(1)-Si(2)}$ 63.6 $^2J_{Si(1)-Si(4)}$ 22.5	−24.6	$^2J_{Si-H}$ 9.1 $^1J_{Si(2)-Si(3)}$ 67.9 $^2J_{Si(2)-Si(4)}$ 33.3	−27.4	$^3J_{Si-H}$ 7.4 $^2J_{Si(3)-Si(5)}$ 33.4
5	I	−75.8	$^1J_{Si-H}$ 246.0	−99.1	$^2J_{Si-H}$ 9.2	−97.8	$^2J_{Si-H}$ 5.5

Table 2. ^{29}Si NMR Data for the 1,3-Dihydrooctahalocyclopentasilanes, 1,3-$H_2Si_5X_8$ (6−8; X = Cl, Br, I)

compd no.	X	Si(1,3)		Si(2)		Si(4,5)	
		δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)
6	Cl	−28.7	$^1J_{Si-H}$ 253.7 $^3J_{Si-H}$ 5.0 $^1J_{Si(1)-Si(5)}$ 75.3 $^2J_{Si(1)-Si(4)}$ 27.0	6.8	$^2J_{Si-H}$ 8.8 $^1J_{Si(2)-Si(3)}$ 75.0 $^2J_{Si(2)-Si(4)}$ 27.0	4.0	$(^2J_{Si-H} + {}^3J_{Si-H})/2$ 9.0
		−29.6	$^1J_{Si-H}$ 254.3 $^3J_{Si-H}$ 5.5 $^1J_{Si(1)-Si(5)}$ 75.6 $^2J_{Si(1)-Si(4)}$ 26.8	5.9	$^2J_{Si-H}$ 7.5 $^1J_{Si(2)-Si(3)}$ 77.0 $^2J_{Si(2)-Si(4)}$ 28.3	3.8	$(^2J_{Si-H} + {}^3J_{Si-H})/2$ 9.2
7	Br	−44.6	$^1J_{Si-H}$ 254.8 $^3J_{Si-H}$ 4.6	−20.7	$^2J_{Si-H}$ 9.3	−22.2	$(^2J_{Si-H} + {}^3J_{Si-H})/2$ 9.2
		−45.5	$^1J_{Si-H}$ 255.0 $^3J_{Si-H}$ 5.7	−21.0	$^2J_{Si-H}$ 8.2	−22.8	$(^2J_{Si-H} + {}^3J_{Si-H})/2$ 9.7
8	I	−77.8	$^1J_{Si-H}$ 244.5	−99.8		−97.3	
		−79.0	$^1J_{Si-H}$ 247.4	−100.3		−97.6	

Table 3. ^{1}H NMR Data for the Nonahalocyclopentasilanes, HSi_5X_9 (3−5; X = Cl, Br, I), and the 1,3-Dihydrooctahalocyclopentasilanes, 1,3-$H_2Si_5X_8$ (6−8; X = Cl, Br, I)

compd no.	formula	δ (ppm)
3	HSi_5Cl_9	4.69
4	HSi_5Br_9	4.55
5	HSi_5I_9	4.98
6	*cis/trans*-1,3-$H_2Si_5Cl_8$	4.72, 4.65
7	*cis/trans*-1,3-$H_2Si_5Br_8$	4.55, 4.46
8	*cis/trans*-1,3-$H_2Si_5I_8$	4.89, 4.75

trans-1,3-$H_2Si_5Ph_8$ (**2**) (Scheme 2). The dearylation of **2** with HX/AlX_3 in benzene led to the formation of equimolar amounts of *cis*- and *trans*-1,3-dihydrooctahalocyclopentasilanes without any silicon-containing byproducts. In the reaction mixture neither the formation of perhalogenated cyclopentasilanes nor the formation of nonahalocyclopentasilanes could be observed. In contrast to nonaphenylcyclopentasilane (**1**), *trans*-1,3-dihydrooctaphenylcyclopentasilane (**2**) could be halogenated without hydrogen being replaced by halogen substitutents. As far as the *cis/trans*-isomers are concerned, a separation by means of crystallization could not be achieved. Thus the pairs of NMR signals (chemical shifts) of **6**−**8** given in Tables 2 and 3 could not be individually assigned to the two diastereomers. The Si−H coupling pattern for Si(4,5) of **6** and **7** (a triplet) has to be classified as a case of a degenerate ABX spectrum.[11] In the case that $\nu_A = \nu_B$, only the sum $|J_{AX} + J_{BX}|/2$ can be obtained from the spectrum. Due to the low solubility of **8** the effective coupling constant $|^3J_{Si-H} + {}^2J_{Si-H}|/2$ could not be observed for this compound as the signal to noise ratio was very low even when a considerable number of FID's were accumulated. The two outer lines of the triplet were undistinguishable from the noise, as was also the case for the signal of Si(2).

In order to synthesize halogenated cyclopentasilanes simultaneously containing different halogen substitutents, we made several attempts to dearylate the fluorinated phenyl cyclopentasilanes FSi_5Ph_9 and *trans*-1,3-$F_2Si_5Ph_8$ in analogy to the halogenation of **1** and **2**. The reasons for the choice of fluorinated educts are the comparatively high stability of Si−F bonds, the anticipation of easily detectable Si−F NMR coupling patterns, and the intention to investigate the molecular dynamics of perhalogenated cyclopentasilanes by means of temperature-dependent ^{19}F-NMR experiments. A number of experiments using liquid hydrogen halides under pressure in sealed heavy-wall NMR tubes as well as HX/AlX_3 dissolved in benzene were performed, but the desired cyclopentasilanes $F_nSi_5X_{10-n}$ ($n = 1, 2$; X = Cl, Br, I) could not be detected. Depending on reagents and reaction conditions the NMR spectra of the respective reaction mixture indicated either the incompleteness of dearylation, the formation of Si_5X_{10}, or the decomposition of the cyclosilane. First attempts to synthesize heptahalocyclotetrasilanes were not yet successful either, but the results were more promising than described before. Reaction pathways and conditions suited for the synthesis of heptahalocyclotetrasilanes, HSi_4X_7 and *t*-$BuSi_4X_7$ (*t*-Bu = *tert*-butyl), by dearylation of the corresponding heptaarylcyclotetrasilanes, HSi_4Ar_7 and *t*-$BuSi_4Ar_7$ (Ar = Ph or *p*-Tol),[6] with HX/AlX_3 or with liquid halogen halides under pressure are under investigation.

Experimental Section

General Comment. Since the products are highly sensitive to moisture, all operations were carried out under nitrogen using modified Schlenk techniques. The educts, HSi_5Ph_9 (**1**, 835.38 g mol^{-1}) and *trans*-1,3-$H_2Si_5Ph_8$ (**2**, 795.27 g mol^{-1}) were prepared by dearylation of decaphenylcyclopentasilane with trifluoromethanesulfonic acid and hydrogenation with lithium aluminum hydride as described in a previous paper.[5] Solvents were distilled from potassium. Anhydrous aluminum halides were used as received from commercial suppliers (purity 95−99%). Hydrogen chloride and hydrogen bromide were pur-

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[11] Hoffmann, R. A.; Forsen, S; Gestblom, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: Berlin, 1971; Vol. 5.

chased from AGA (purity > 99.8%). Hydrogen iodide was prepared from tetrahydronaphthalene and elementary iodine.[12]

The NMR measurements were performed on a Bruker 300 MSL spectrometer in C_6D_6. ^{29}Si spectra were recorded at 59.6 MHz, and ^1H spectra at 300.1 MHz. Coupling constants are given as absolute values; the Si−Si coupling constants were measured by means of INADEQUATE pulse sequences.[13] Chemical shifts are reported relative to TMS.

The preparation and characterization of HSi_5Cl_9 (**3**) were performed by Stüger et al.;[4] thus only the NMR data of this compound are given in Table 1.

Nonabromocyclopentasilane (4). **1** (2.5 g, 3.0 mmol) was dissolved in benzene (20 mL) in a round-bottom three-neck flask (100 mL) with magnetic stirrer, reflux cooler, and a gas-inlet tube. The gaseous hydrogen halide was taken from a steel bottle and led through a phosphorus(V) oxide drying tube before entering the gas-inlet tube. After the solution had been saturated with hydrogen bromide, a catalytic amount of $AlBr_3$ (ca. 0.1 g) was added and under vigorous stirring the introduction of HBr was continued. The warming of the reaction mixture and further uptake of HBr indicated the start of the reaction. After 0.5 h an infrared spectrum of the reaction mixture was measured. Since the bands at 997 cm^{-1} and at 1430 cm^{-1}, which are characteristic for phenylated silanes, still could be detected, another portion of $AlBr_3$ was added and the introduction of HBr was continued. This procedure was repeated every 15 min until the IR bands mentioned before could not be detected any more. After 1 h of total reaction time the benzene was removed in vacuo and replaced by heptane (70 mL), and then the catalyst was separated by filtration. After removal of the solvent in vacuo, a highly viscous yellowish oil was obtained. The oil partially solidified in microcrystalline structures (yield 2.4 g, 93%). Besides HSi_5Br_9 (**4**) the product contained 10−20% Si_5Br_{10}, which could not be separated by crystallization or sublimation.

Data: M_r 759.29 g mol^{-1}; IR (cm^{-1}) 2151 m, 867 m, 841 m, 819 s, 780 vw, 769 vw, 740 vw, 712 s, 695 sh, 646 m, 607 vw, 528 s, 515 vw, 503 sh, 490 s, 471 vs, 403 s, 361 m, 325 s, 292 s, 283 s.

Nonaiodocyclopentasilane (5). **1** (3.2 g, 3.8 mmol) was dissolved in benzene (20 mL). The reaction was performed in analogy to the preparation of **4** using HI instead of HBr and AlI_3 instead of $AlBr_3$. Due to the low solubility of HSi_5I_9 the reaction mixture opacified increasingly in the course of the reaction. After the addition of three portions of AlI_3 and 2 h of HI introduction, the IR spectrum of the mixture indicated that all the phenyl substituents had been replaced by iodine. The benzene was removed in vacuo. and the residue was digested by a mixture of heptane (69 mL) and toluene (20 mL). After filtration the solvents were removed in vacuo. The product precipitated as a yellowish/white crystalline solid (yield 2.9 g, 59%). Besides HSi_5I_9 it contained about 10% of Si_5I_{10}, which could not be separated by crystallization or sublimation.

Data: M_r 1283.58 g mol^{-1}; IR (cm^{-1}) 2147 m, 724 vs, 694 w, 676 wb, 638 m, 490 s, 475 s, 458 s, 420 vw, 394 vs, 357 w, 340 s, 321 vw, 314 vw, 303 m, 289 w, 277 s, 273 s.

1,3-Dihydrooctachlorocyclopentasilane (6). **2** (2.3 g, 2.9 mmol) was dissolved in benzene (20 mL). The reaction was performed in analogy to the preparation of **4** using HCl instead of HBr and HCl instead of $AlBr_3$. After 0.5 h of $AlCl_3$ introduction, the IR spectrum indicated the completeness of halogenation. The benzene was removed in vacuo and replaced by heptane (70 mL). After filtration the solvent was removed in vacuo and a yellowish, highly viscous oil was obtained. The oil partially solidified in microcrystalline structures (yield 1.2 g, 97%). No products other than *trans*-1,3-$H_2Si_5Cl_8$ (**6a**) and *cis*-1,3-$H_2Si_5Cl_8$ (**6b**) in equimolar amounts were detected.

Data: M_r 426.07 g mol^{-1}; IR (cm^{-1}) 2161 m, 738 s, 729 sh, 684 w, 575 vs, 559 sh, 548 sh, 520 s, 483 wb, 472 sh, 408 m, 402 sh, 358 m, 352 sh.

1,3-Dihydrooctabromocyclopentasilane (7). **2** (1.5 g, 1.9 mmol) was dissolved in benzene (20 mL). The reaction was performed in analogy to the preparation of **4**. After the addition of two portions of $AlBr_3$ and 1 h of HBr introduction, the IR spectrum indicated the completeness of halogenation. The benzene was removed in vacuo and replaced by heptane (70 mL). After filtration the solvent was removed in vacuo and a yellowish, highly viscous oil was obtained. The oil partially solidified in microcrystalline structures (yield 1.3 g, 88%). No products other than *trans*-1,3-$H_2Si_5Br_8$ and *cis*-1,3-$H_2Si_5Br_8$ in equimolar amounts were detected.

Data: M_r 781.68 g mol^{-1}; IR (cm^{-1}) 2165 m, 904 w, 874 vw, 843 vw, 820 vw, 771 w, 743 vw, 715 s, 700 sh, 669 m, 483 s, 466 vs, 406 s, 379 vw, 357 w, 338 m, 329 sh.

1,3-Dihydrooctaiodocyclopentasilane (8). **2** (1.0 g, 2.9 mmol) was dissolved in benzene (20 mL). The reaction was performed in analogy to the preparation of **4** using HI instead of HBr and AlI_3 instead of $AlBr_3$. The solvent started to reflux soon after the addition of the first portion of catalyst. After 0.5 h of HI introduction, the IR spectrum indicated the completeness of halogenation. Due to the low solubility of $H_2Si_5I_8$ the catalyst was not separated by filtration. The solvent was removed in vacuo, and the crude product was obtained as a yellowish, highly viscous oil, which partially solidified in microcrystalline structures (1.2 g, 105%, the surplus is due to the catalyst). No silicon-containing products other than *trans*-1,3-$H_2Si_5I_8$ and *cis*-1,3-$H_2Si_5I_8$ in equimolar amounts were detected.

Data: M_r 1157.68 g mol^{-1}; IR (cm^{-1}) 2140 w, 723 w, 674 s, 643 s, 608 m, 496 m, 470 s, 452 s, 387 vs, 339 s, 281 s.

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